CONCLUSIONS

There are three parts of the experiment: first, experimental factors screening and optimization of copyrolsis reaction between PVC and cattle manure; second, study of kinetic behavior of this reaction; and third, upgrading of the copyrolyzed oil from copyrolysis of PVC-containing plastic mixture and cattle manure by silica alumina-iron oxide and silica alumina-zinc oxide composite catalysts.

Experimental factors: heating rate, reaction temperature, holding time and PVC:cattle manure ratios were screened by 2^k factorial design. Heating rate and reaction temperature had significant effects on HCl reduction in reliability of 95%. However, interaction plot showed the ratio of PVC to cattle manure had interaction with the other two factors while holding time had no interaction with others. Therefore, only holding time was screened in this consideration, the holding time of 60 min provided the best result. After screening experimental factors, three factors: heating rate, reaction temperature, and the ratio of PVC to cattle manure were optimized by Box-Behnken model. The Box-Behnken design showed the best conditions of HCl reduction at low heating rate of 1°C/min and high reaction temperature of 450°C. In the statistical method, reliability of the model was R^2=92.2% and lack of fit was 85% reliability, therefore, these results are acceptable. From experimental results, the PVC:cattle manure ratio of 1:5, 450^{o}C, and 1^{o}C/min provided the highest HCl reduction, therefore, these are the optimum conditions.

The optimum conditions were applied to PVC-containing plastic mixture. Synergistic effect showed that cattle manure the decreased the liquid yield by 17% but increased the solid and gas by 25% and 14%, respectively. Cattle manure provided an increase in cracking activity, resulting in more gas product, and some intermediates were polymerized to larger molecules in solid yield. Cracking activity from cattle manure also affected the distilled product, gasoline was nearly 60%. Gasoline fraction showed a decrease in the total concentration of benzene, toluene, and xylene from 2.46mol/l (no cattle manure) to 0.93mol/l (with cattle manure) and chlorine from PVC in plastic mixture was reduced by 45%. The octane numbers of copyrolyzed oil were not much different (>95). Therefore, copyrolyzed oil from copyrolysis of cattle manure and PVC-containing plastic mixture had good quality and environmental friendly.

The second part was the study of kinetic behavior of copyrolysis reaction between PVC and cattle manure. This result was used to support the results from the first part. The kinetic parameters of Arrhenius equation: activation energy, reaction order, and pre-exponential factor were investigated by isothermal and dynamic methods. The activation energy reduced when the amount of cattle manure was increased. Cattle manure eased the decomposition due to reductions of activation energy, and also the pre-exponential factor. The reaction orders from both isothermal and dynamic measurements decreased when cattle manure was increased three times the amount of PVC. However, cattle manure five times the amount of PVC did not affect the reaction order from both methods but decreased the rates of dechlorination and decomposition.

Even though the copyrolyzed oil had small amount of chlorine, the chlorine in oil should be reduced to nearly zero. Therefore, the last part was the study of upgrading the copyrolyzed oil from copyrolysis of PVC-containing plastic mixture and cattle manure at optimum conditions by silica alumina-iron oxide and silica alumina-zinc oxide. Both silica alumina-iron oxide and silica alumina-ZnO catalysts showed higher cracking activity than silica alumina, and these composite catalysts gave iso-paraffin structure which provided high octane number. However, silica alumina-ZnO composite catalyst could reduce chlorine in oil more than silica alumina-Fe_2O_3 composite catalyst, so ZnO composite catalyst was chosen for upgrading the copyrolyzed oil. The effects of ratios of silica alumina to ZnO were studied. The increase amount of ZnO gave higher cracking activity. The appropriate silica alumina:ZnO ratio was 1:1 because it provided the lowest chlorine content in oil, high iso-paraffin and high octane number. The retention time in the reactor is also an important factor. There were three feed rates in the study: 10, 30, and 50 ml/h. The optimum feed rate was 30 ml/h because it gave high gasoline fraction and the lowest chlorine content in the oil.